Integrated multiscale model for design of robust 3-D solid-state lithium batteries

2022 Vehicle Technologies Office Annual Merit Review

June 21-23, 2022

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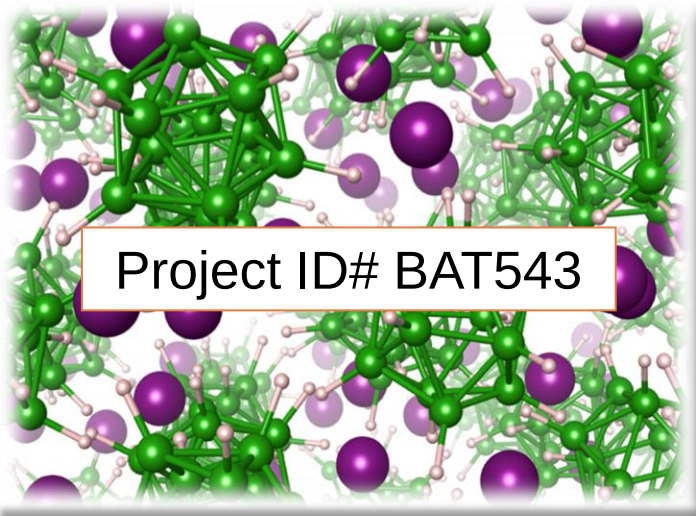
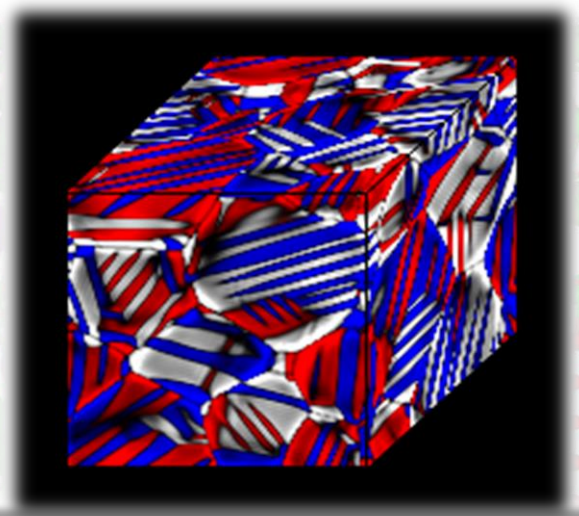
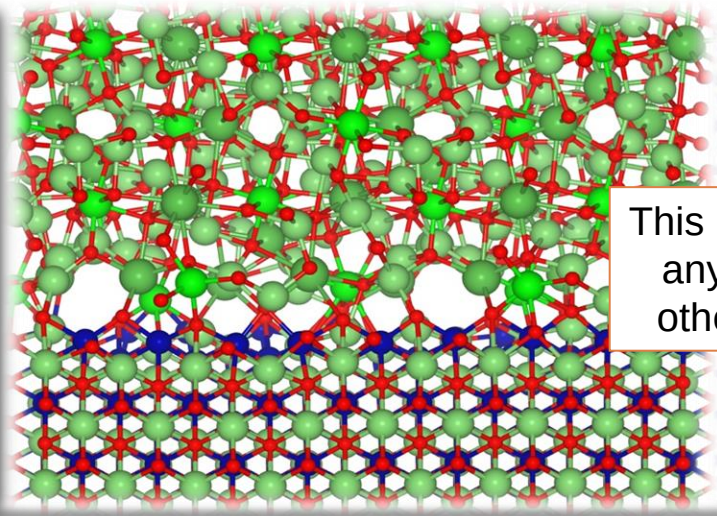


Project ID# BAT543





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LLNL-PRES-XXXXXX

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 11/1/2021

Project end date: 10/30/2024

Barriers addressed

- **Performance (Barrier B):** Chemo-mechanical effects on performance
- **Life (Barrier C):** Poor battery cyclability due to interfacial chemical reactions

Budget

Total project funding: $1,125K (DOE share)

New FY22 funding: $375K

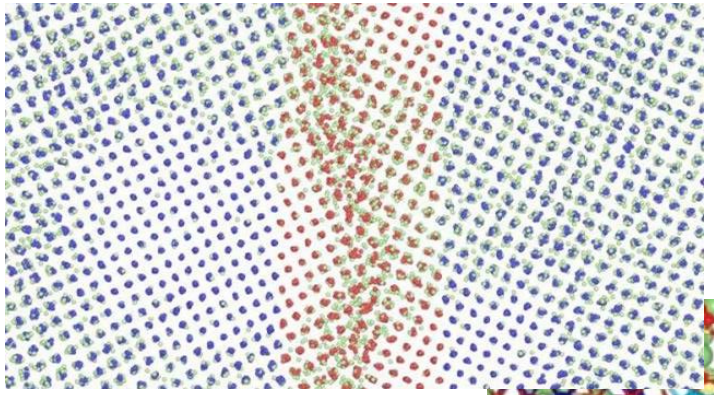
Partners

Collaboration with Project # BAT539
"3D Printing of Solid-state Li Batteries" (PI: Jianchao Ye, LLNL)

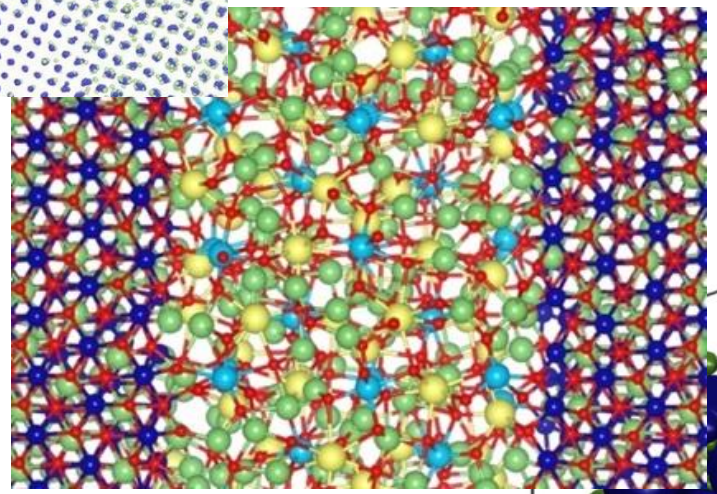
Collaboration with U.S.-Germany partnership on solid-state batteries: Cathode/electrolyte interface (CatSE)

Relevance: Interfaces in solid-state batteries dictate key properties

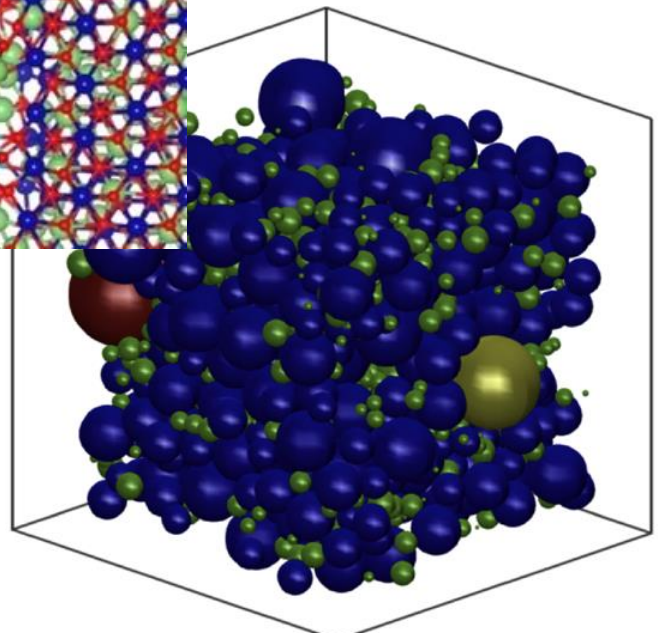
Grain boundaries



Interphase boundaries

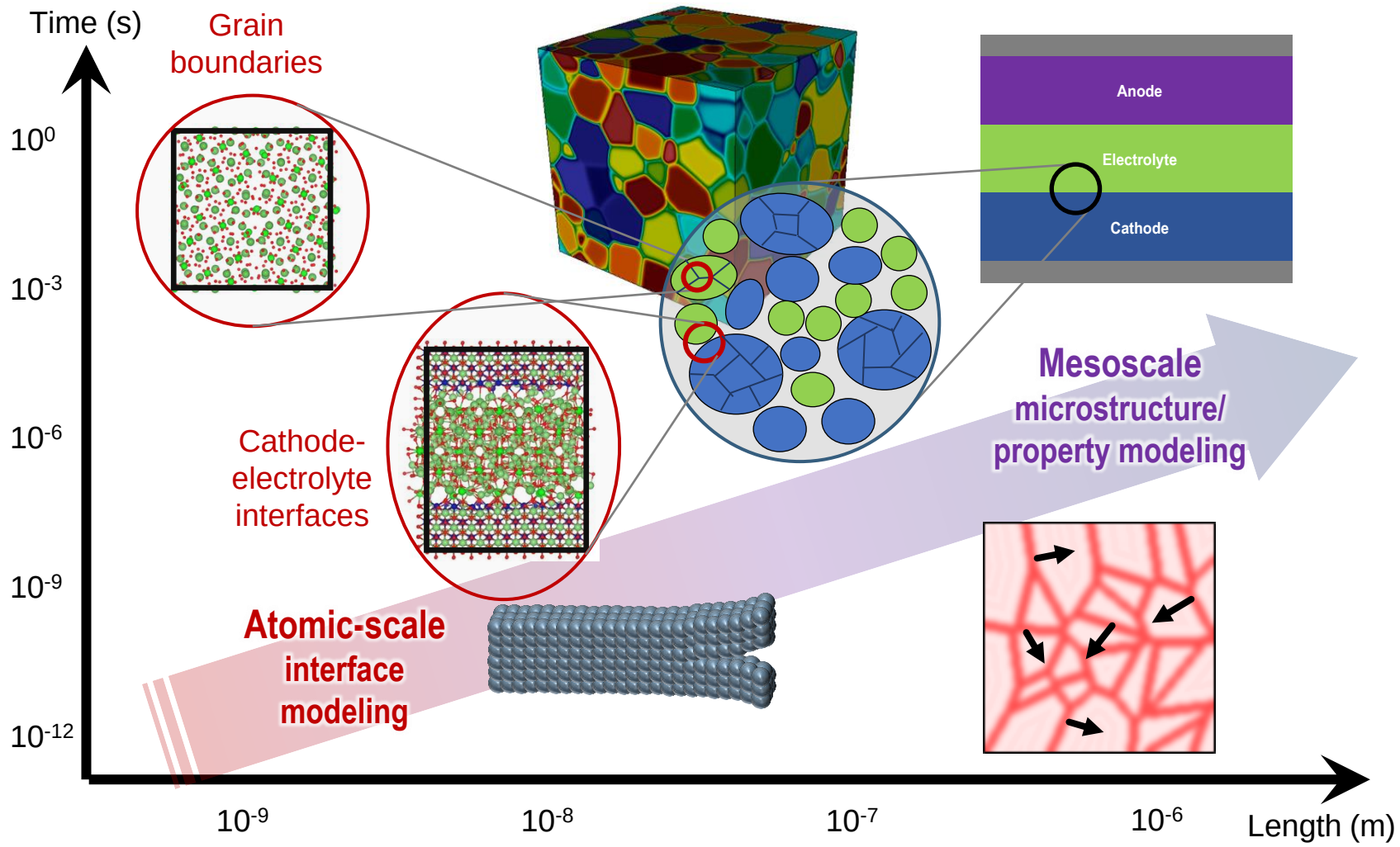


Interparticle interfaces



- Transport
- Mechanics
- Stability
- Processability

Approach: Multiscale modeling of ion transport across interfaces



DFT calculations	***Molecular dynamics***	***Effective-medium***	***Phase-field***
of bond breaking energetics	*simulations of crack formation*	*simulations of stress distributions*	*simulations of lithiation/cycling*

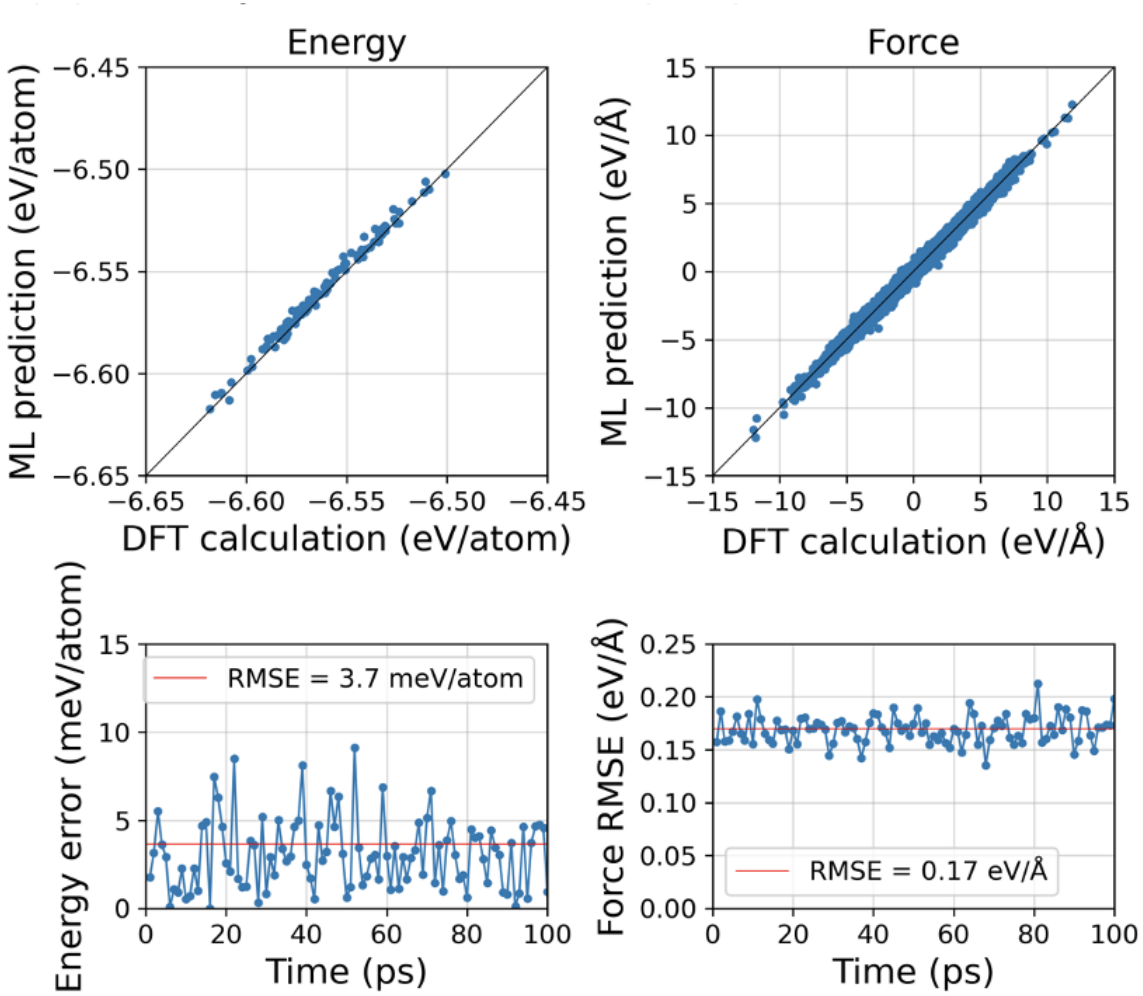
Progress towards project milestones

Month/Year	Description of Milestone	Status
January 2022	Complete atomistic cathode-electrolyte interface models	50 % complete
April 2022	Determine composition profiles of cathode-electrolyte interfaces	50% complete
July 2022	Set up model for local stress mapping	0 % complete
October 2022	Train machine learning force fields for disordered interfaces	100 % complete

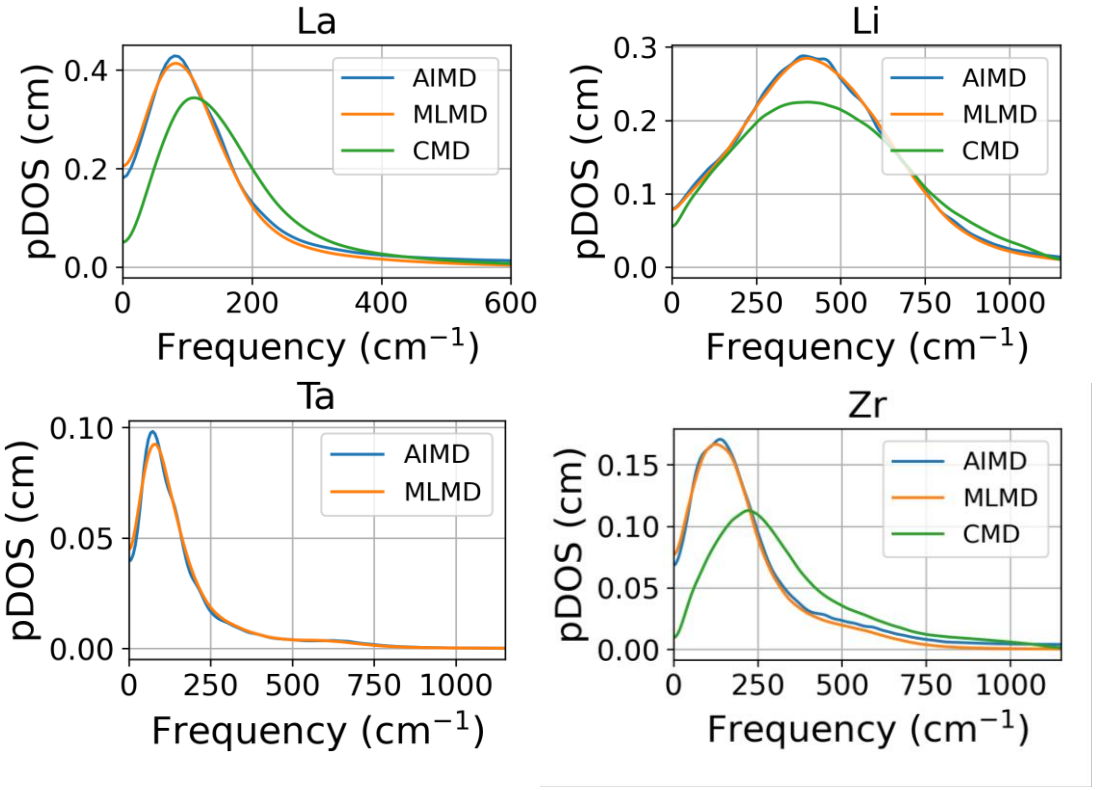
Decision was made to prioritize the machine-learning development work for accelerating future interface simulations and providing inputs for the US-Germany collaboration.

Accomplishment: Validated machine-learning force field (MLFF) for LLZO

We trained and validated efficient MLFFs to accelerate simulations of pristine and doped LLZO with quantum accuracy



Phonon density of states

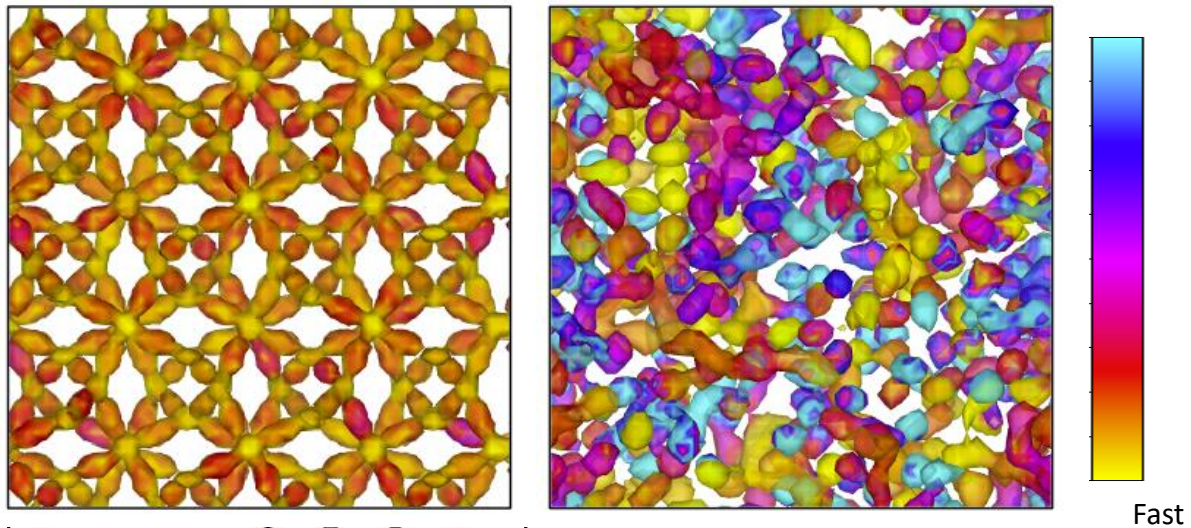


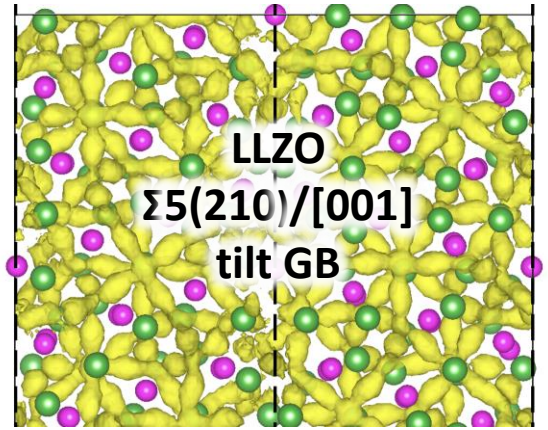
Demonstrated high accuracy for Ta, Ba, Al dopants and for disordered LLZO will enable evaluation of mechanical and transport implications of solute segregation at grain boundaries

Accomplishment: Thermomechanical property predictions for LLZO using MLFF

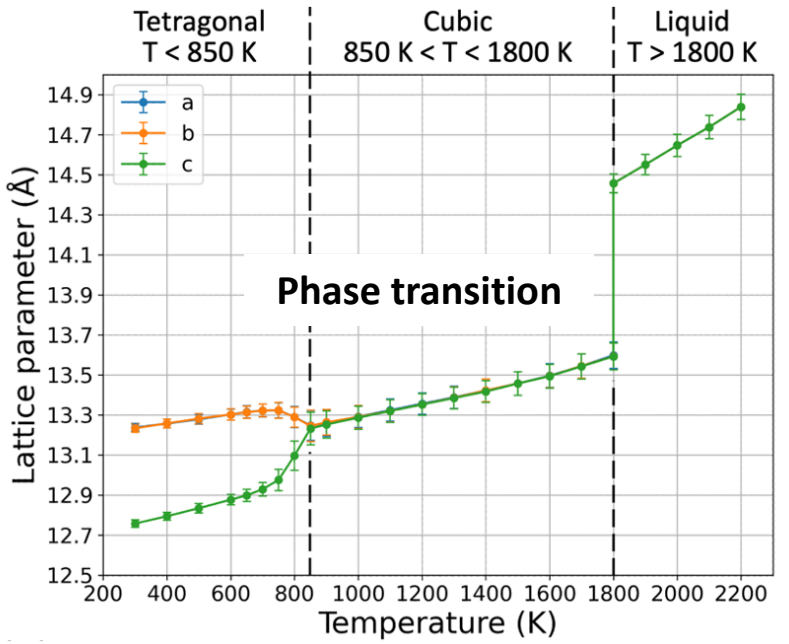
MLFFs were used to examine coupling between stress, disorder, ion transport, and phase stability of LLZO

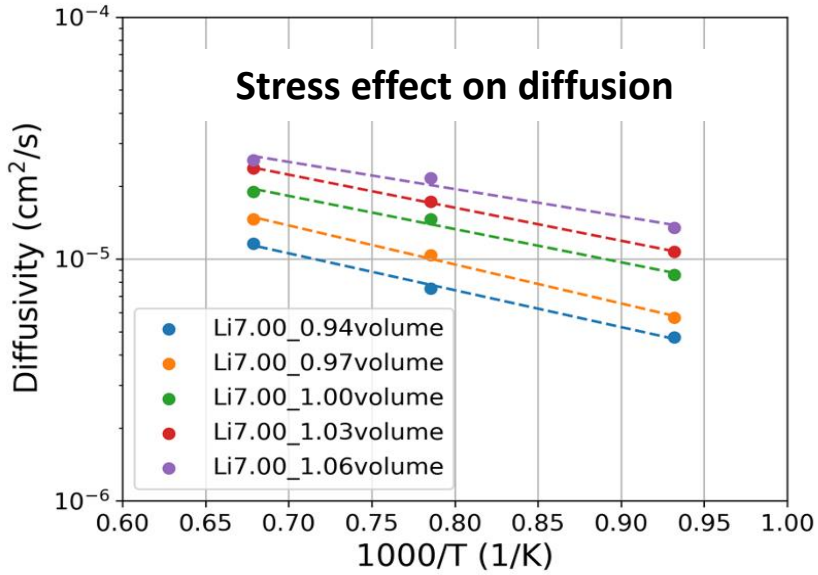
Crystalline LLZO **Disordered LLZO/high-angle GB**





Simulations predict that disorder and stress at interfaces significantly decrease overall permeability and homogeneity of ion transport in polycrystalline LLZO

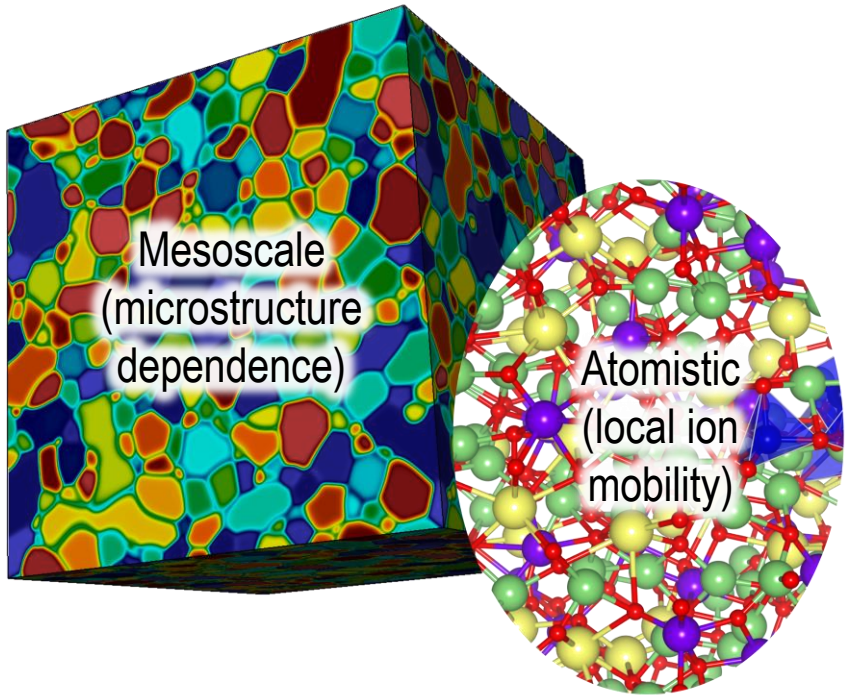


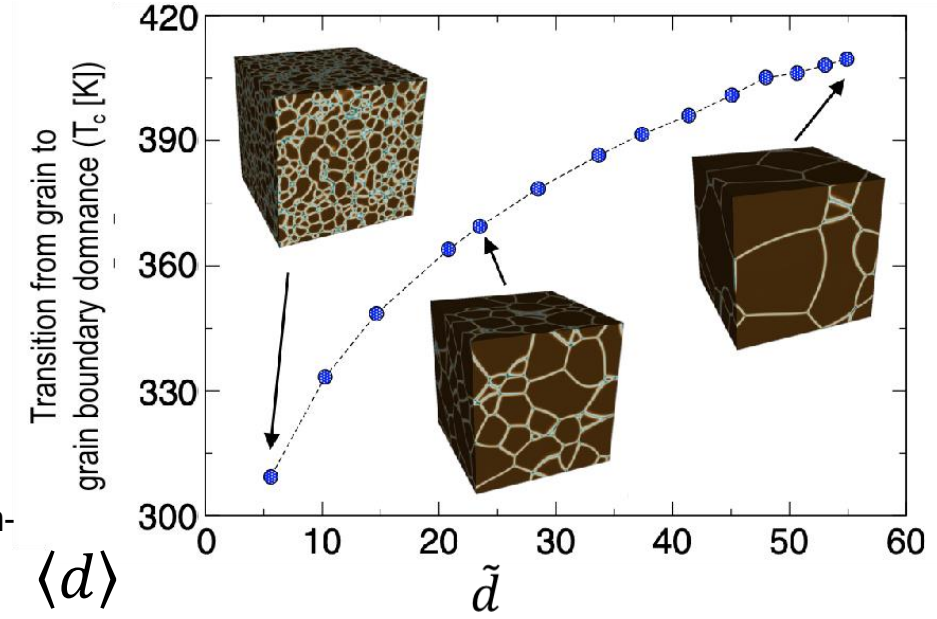


Kim et al., *in review* (2022)

Accomplishment: Impact of grain structure on Li^+ transport

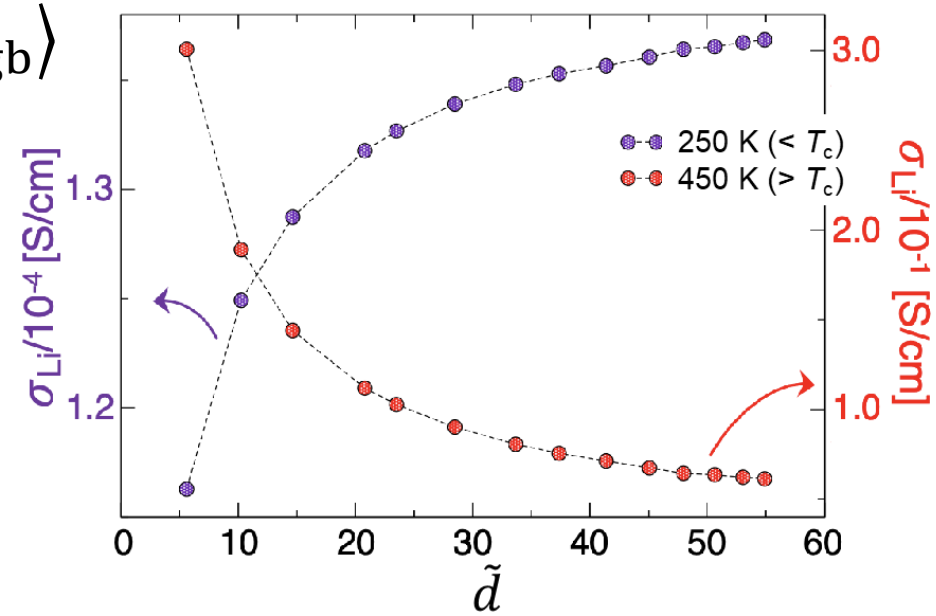
Integrated atomistic-mesoscale model was used to determine relationship between temperature, microstructure, and transport in polycrystalline Li^+





Dimension-less size

$$\tilde{d} = \frac{\langle d \rangle}{\langle l_{gb} \rangle}$$



- **Relationship between T_c and operating temperature determines whether GBs are blocking or beneficial**
- **Currently investigating possible connection to critical current density for dendrite formation**

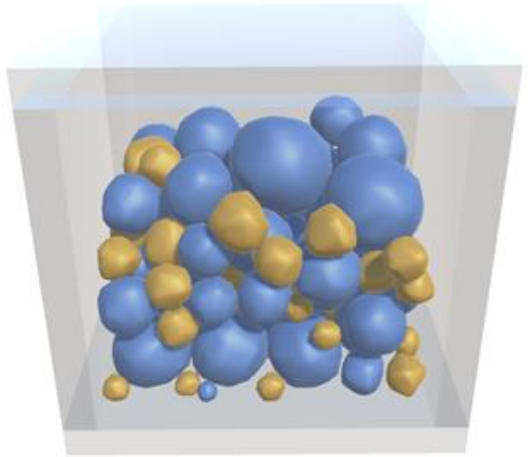
T.W. Heo et al., *npj Comp. Mater.* **7**, *214* (2021)

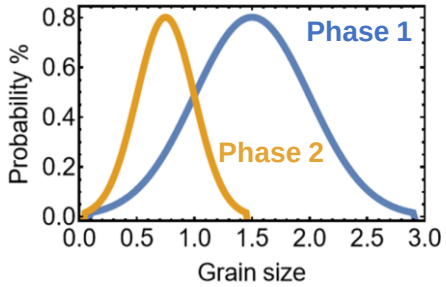
Accomplishment: Computational workflow for multiparticle LLZO-cathode composites

New mesoscale modeling framework can compute composition and stress distributions in complex, multiphasic and multiparticle mixtures of LLZO-cathode composites

Microstructure generation with controlled grain/particle size distributions

A stack of particles created by open-source software *Particula*

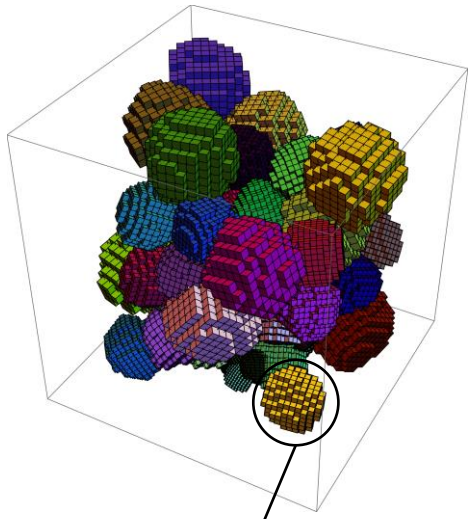


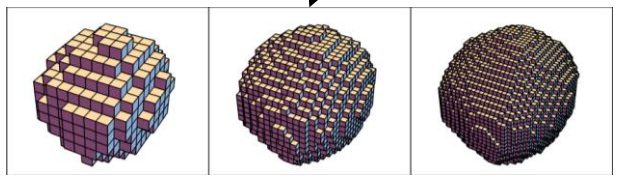


Controlled grain size distributions for each phase

format conversion

Voxelized microstructure to be readable by our *MesoMicro* code



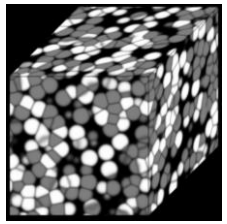


Resolution 10^3 Resolution 20^3 Resolution 30^3

Controlled voxel resolution for each grain

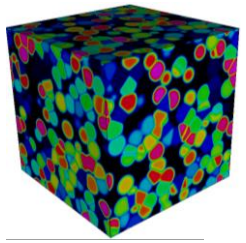
Diffusion solver with chemomechanical coupling

Simulation of time-dependent Li-ion transport and calculation of effective properties

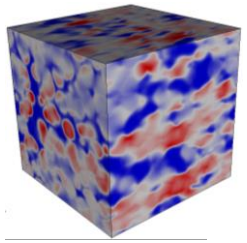


Phases

Composition C_{Li}



Grain orientation



Stress σ_{ij}

$$\partial_t C_{\mathrm{Li}} = \nabla(\mathbf{D}(\boldsymbol{x})\nabla C_{\mathrm{Li}} + (\mathbf{M}(\boldsymbol{x})\nabla\boldsymbol{\sigma}(\boldsymbol{x}))C_{\mathrm{Li}})$$

diffusion driven by concentration gradients

"drift" driven by stress gradients

$$\nabla\boldsymbol{\sigma}(C_{\mathrm{Li}}(\boldsymbol{x})) = 0$$

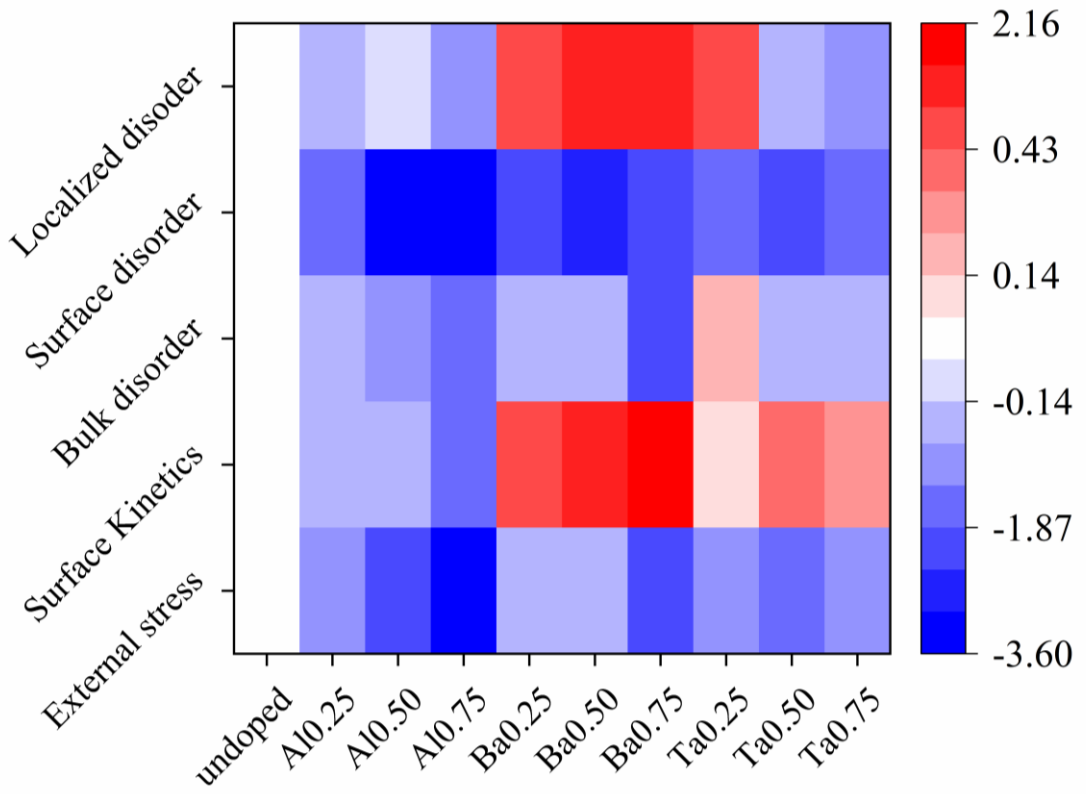
mechanical equilibrium with chemical strains

Solving transport equations with self-consistent chemo-mechanical coupling

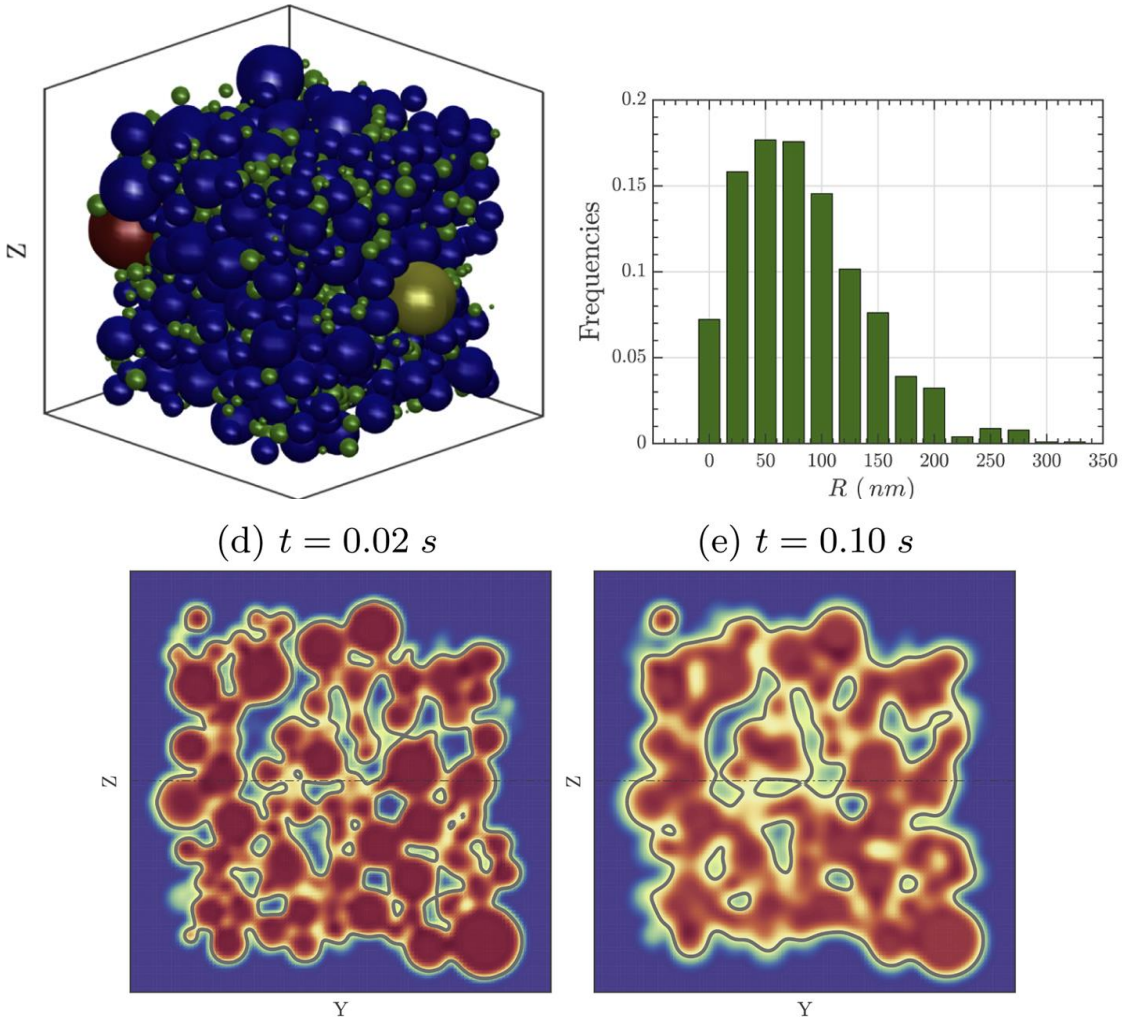
Accomplishment: Effects of LLZO sintering from multiscale simulations

Ab initio calculations and mesoscale simulations probe ease of sintering with composition and microstructure

Metrics to compare qualitative ease of sintering



Green body formulation to compare the effects of particle size and distribution



Collaborations

Dr. Jianchao Ye, LLNL (Project # BAT539: “3D printing of solid-state batteries”)

- *Analysis of 3D printed/sintered structures for informing microstructure models*
- *Interpreting effects of processing on microstructure and diffusivity*

Prof. Nicole Adelstein, San Francisco State University

- *Methods for simulating diffusion of Li^+ in disordered garnet and halide solid-state electrolytes*
- *Benchmarking classical and machine learning interatomic potentials*

U.S.-Germany collaboration on solid-state battery research

- *Timo Danner, Arnulf Latz, Katharina Becker-Steinberger, Jan Dippel, DLR: Modeling microstructure effects of the solid-state electrolytes on ionic conductivity*
- *Eric Wachsman, U. Maryland; Dina Fattakhova, Jülich; Jeff Sakamoto, U. Michigan: Synthesis and characterization of polygranular electrolytes*

Publications & presentations

- T.W. Heo, A. Grieder, B. Wang, M. Wood, T. Hsu, S. Akhade, L.F. Wan, L.-Q. Chen, N. Adelstein, and B.C. Wood, "Microstructural impacts on the ionic conductivity of oxide-based solid electrolytes: A combined atomistic-mesoscale approach," npj Comp. Mater. (2021), 7, 214.
- K. Kim, D. Park, H.-G. Jung, K.Y. Chung, J.H. Shim, B.C. Wood, and S. Yu, "Materials design strategy for halide solid electrolytes Li_3MX_6 (X=Cl, Br, I) for all-solid-state high-voltage Li-ion batteries," Chem. Mater. (2021), 33, 3669.
- B.C. Wood, J.B. Varley, K.E. Kweon, P. Shea, A.T. Hall, A. Grieder, M. Ward, V.P. Aguirre, D. Ringling, E.L. Ventura, C. Stancill, and N. Adelstein, "Paradigms of frustration in superionic solid electrolytes," Phil. Trans. R. Soc. A 379, 20190467 (2021) [invited].
- Z. Mehmedovic, V. Wei, A. Grieder, P. Shea, B.C. Wood, and N. Adelstein, "Impacts of vacancy-induced polarization and distortion on diffusion in solid electrolyte Li_3OCl," Phil. Trans. R. Soc. A 379, 20190459 (2021) [invited].
- D. Park, K. Kim, G.H. Chun, B.C. Wood, J.H. Shim, and S. Yu, "Materials design of sodium chloride solid electrolytes Na_3MCl_6 for all-solid-state sodium-ion batteries," J. Mater. Chem. A 9, 23037 (2021).
- R. Shi, M. Wood, T.W. Heo, B.C. Wood, and J. Ye, "Towards understanding particle rigid-body motion during solid-state sintering," J. Eur. Ceram. Soc. 41, 211 (2021).
- K. Kim, A. Dive, A. Grieder, N. Adelstein, S. Kang, L. F. Wan and B.C. Wood, "Development of machine-learning interatomic potential for crystalline/amorphous $Li_7La_3Zr_2O_{12}$ solid electrolyte for solid-state batteries," submitted (2022).
- L.F. Wan, "Elucidating interfacial instability in all-solid-state lithium batteries from first-principles simulations", MRS Spring Meeting, Virtual (April 2021).
- B.C. Wood, "Understanding interfaces and interfacial ion conduction in LLZO from multiscale simulations," 3rd World Conference on Solid Electrolytes for Advanced Applications: Garnets and Competitors, Virtual (October 2021) [invited].

Remaining challenges & barriers

Atomic-scale simulations of interface remain limited to short timescales

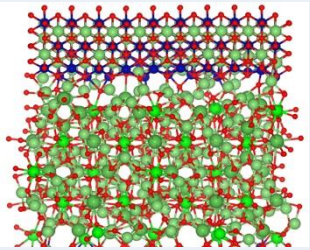
- *Continue to push the limit of simulation time and lengthscale using MLFF*
- *Focus on understanding relationship between local chemistry/structure and transport rather than mimic realistic long-time evolution of interfacial chemistry*

Comparison and validation with experimental studies may prove challenging

- *We are working with collaborators through the U.S.-Germany solid-state battery partnership to experimentally validate our models*
- *We are connecting our models with larger-scale simulation techniques through the U.S.-Germany partnership to incorporate realistic electrode-electrolyte composite formulations from tomography*

Proposed future work

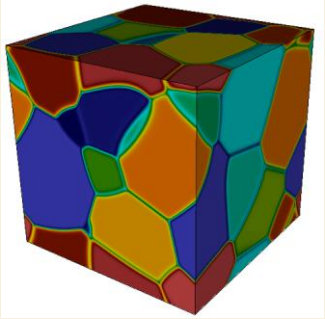
Atomistic



Cathode-electrolyte interface

- Compare the intrinsic mechanical properties of garnet and halide electrolytes
- Evaluate the effects of doping on the chemo-mechanical response at the interface
- Determine threshold stress for bond breaking at the interface

Mesoscale



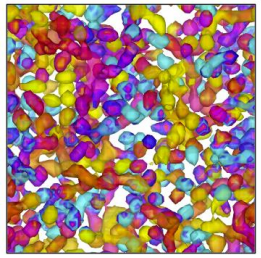
Mechanical stress effects on ion transport

- Complete simulations and quantitative analysis of the stress effect on Li ion transport through complex solid-electrolyte microstructures

Composite electrolyte microstructures

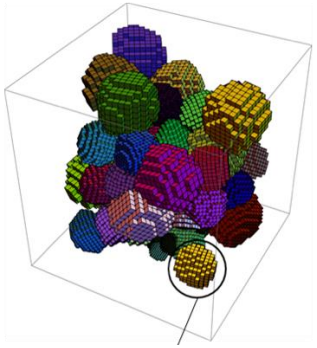
- Apply new mesoscale modeling scheme to analyze composite polymer-ceramic microstructure effects on Li ion transport and mechanics (collaboration with experimental project BAT539, J. Ye)

Summary



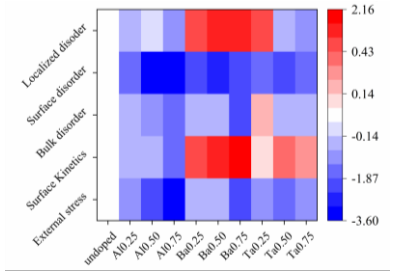
Successfully leveraged machine learning to accelerate atomic-scale simulations

- Validated approach can incorporate disorder, doping, and stress to evaluate interfacial effects
- Early results demonstrate significant effects of physicochemical factors on transport at interfaces



Developed approach to simulate complex electrolyte-cathode composites

- Mesoscale model will be used to compute effective mechanical and transport properties of realistic composites



Connected properties to processing

- Multiscale simulations aid understanding of how composition and green body microstructure affect sintering behavior and processability